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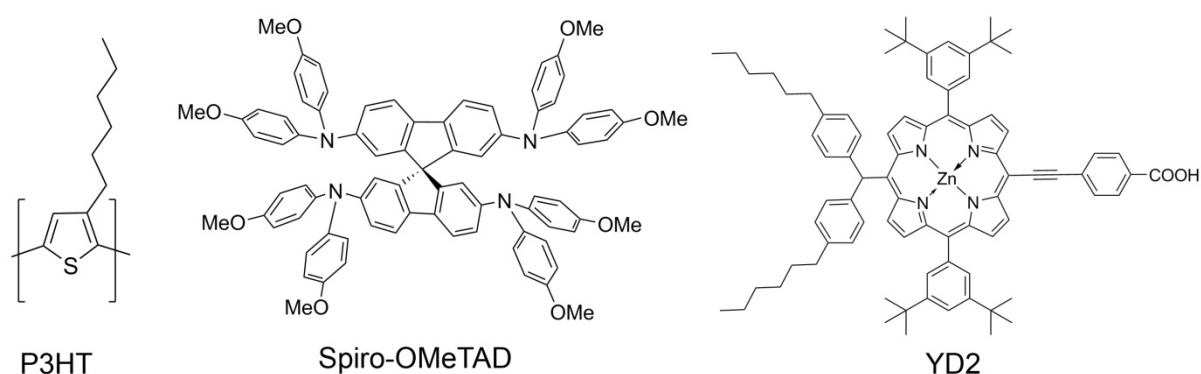
Enhanced light harvesting in mesoporous TiO<sub>2</sub>/P3HT hybrid solar cells using a porphyrin dye

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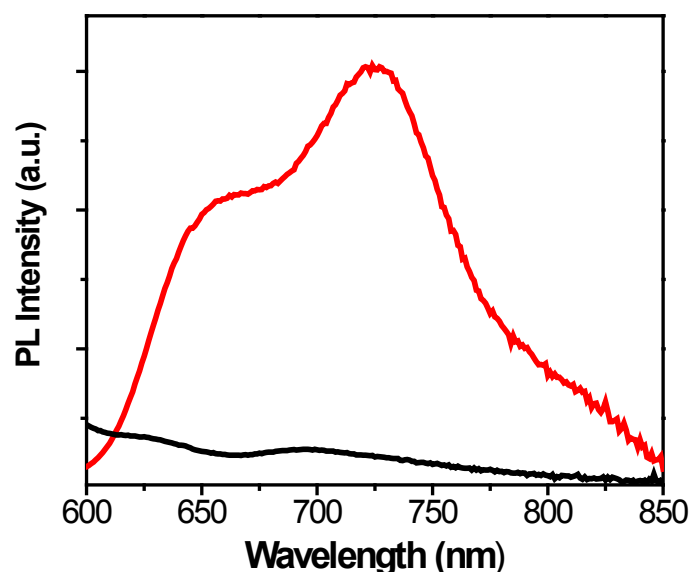
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**Fig. S1.** The molecular structures of the P3HT, Spiro-OMeTAD and YD2 are shown.

**Table S1.** Photovoltaic performance of YD2 sensitized cells with Spiro-OMeTAD and P3HT. Measured under AM1.5 conditions, 100 mW/cm<sup>2</sup>. (0.20 cm<sup>2</sup> of masked active area)

Device	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	$F.F.$	$\eta$ (%)
TiO <sub>2</sub> /P3HT	2.12	425	0.53	0.49
TiO <sub>2</sub> /YD2/P3HT	12.1	510	0.50	3.13
TiO <sub>2</sub> /YD2/P3HT (duplicate)	10.62	534	0.53	3.03
TiO <sub>2</sub> /YD2/Spiro-OMeTAD	2.56	827	0.77	1.64



**Fig. S2.** Photoluminescence spectra of the pristine P3HT film (red) and P3HT/YD2 mixture (black).

#### Device fabrication details:

The fabrication of our hybrid solar cells employed a F-doped  $\text{SnO}_2$  glass substrate ( $15\Omega/\square$ , Pilkington) onto which a  $\sim 100$  nm compact  $\text{TiO}_2$  layer was deposited by spray pyrolysis.<sup>1</sup> Since P3HT is known to have difficulties infiltrating the 20 nm pores traditionally used in  $\text{TiO}_2$ -based solar cells,<sup>2</sup> we prepared our mesoporous  $\text{TiO}_2$  layer with larger particles and larger pores. A layer about 1  $\mu\text{m}$  thick with 75 nm  $\text{TiO}_2$  particles was coated onto the FTO/compact  $\text{TiO}_2$  substrate using the spin coater. The 75 nm powder was received from Showa Titanium Co., and the  $\text{TiO}_2$  paste was prepared using a previously reported procedure.<sup>3</sup> The electrode was then annealed at 500  $^\circ\text{C}$  for 30 min under oxygen flow, followed by treatment with a 0.02 M  $\text{TiCl}_4$  aqueous solution for 6 hours at room temperature. It was re-annealed at 450  $^\circ\text{C}$  in air for 30 min and cooled before immersing it into a YD2 dye solution (0.2 mM in ethanol with 0.4 mM chenodeoxycholic acid to prevent aggregation<sup>4</sup>) for 18 hours. The dye coated  $\text{TiO}_2$  electrodes were spin-coated at 250 rpm for 500 sec with a regioregular-P3HT solution (Reike Metals Co. 30 mg/ml in chlorobenzene). A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) solution (2.8 wt% dispersion in water, Baytron P) diluted with two volumes of MeOH was spin-coated onto the  $\text{TiO}_2$ /YD2/P3HT films at 2000 rpm for 30 sec. As a counter electrode, Au was deposited on top of the samples using thermal resistance evaporation to define an active device area of 0.20  $\text{cm}^2$ . To compare the  $\text{TiO}_2$ /YD2/P3HT based devices to devices without the benefit of the panchromatic light absorption, two types of control devices were prepared. First  $\text{TiO}_2$ /P3HT devices were prepared as above, but without the YD2 dye. Also, a YD2 sensitized  $\text{TiO}_2$  device with the transparent HTM, Spiro-OMeTAD, was assembled under optimized conditions as previously described.<sup>5</sup> In this case the mesoporous  $\text{TiO}_2$  layer had a thickness of 2  $\mu\text{m}$

with 20 nm particles as this morphology has been found to give the highest performance in Spiro-OMeTAD based devices.

Additional experimental details:

*Device characterization:* The incident photon-to-current conversion efficiency (IPCE) was created by using the incident light from a 300 W xenon lamp (ILC Technology, U.S.A.), which had been focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). The irradiation source employed for the *J-V* measurements was a filtered (Schott 113) 450 W xenon light source (Osram XBO 450, USA) whose power was adjusted using a reference Si photodiode equipped with a color-matched filter (KG-3, Schott), thus reducing the spectral mismatch between the simulated light and AM 1.5G irradiation in the region of 350–750 nm to less than 4%.

*PL Measurements:* To probe efficient electron transfer from P3HT to YD2, photoluminescence (PL) measurements were performed using a time-correlated single photon counting (TCSPC) system from PicoQuant. Films were excited with a pulsed laser diode, (model LDH 485: 481nm, 70ps FWHM, 5MHz) detected with a single photon avalanche diode (PDM 100CT SPAD) attached to a monochromator and processed by a PicoHarp 300 correlating system. For the PL measurements we deposited the pristine P3HT and the P3HT/YD2 (P3HT:YD2=20:1 concentration ratio) in an inert poly(methyl methacrylate) (PMMA) matrix on a glass substrate using a spin coater.

References:

1. L. Kavan and M. Grätzel, *Electrochim. Acta*, 1995, **40**, 643-652.
2. K. M. Coakley and M. D. McGehee, *Appl. Phys. Lett.*, 2003, **83**, 3380-3382.
3. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovoltaics Res. Appl.*, 2007, **15**, 603-612.
4. A. Kay and M. Graetzel, *J. Phys. Chem.*, 1993, **97**, 6272-6277.
5. S.-J. Moon, J.-H. Yum, R. Humphry-Baker, K. M. Karlsson, D. P. Hagberg, T. Marinado, A. Hagfeldt, L. Sun, M. Grätzel and M. K. Nazeeruddin, *J. Phys. Chem. C*, 2009, **113**, 16816-16820.